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Formulation and Make-Up of Simulated Dilute Water, Low Ionic Content Aqueous Solution

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Lawrence Livermore National Laboratory

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University of California **Lawrence Livermore National Laboratory** **YUCCA MOUNTAIN PROJECT** **Technical Implementing Procedure**	**No.:** TIP-CM-06 **Revision:** CN TIP-CM-06-0-2 **Effective Date:** 04/04/97 **Page:** 1 of 7
Subject: Formulation and Make-Up of Simulated Dilute Water, Low Ionic Content Aqueous Solution	**AUTHOR:** G. Gdowski

Training Required: Yes ■ No ☐

Comments:

Addition of balance to acceptable list in Section 6.0; changes made in Procedure

REVISION HISTORY

Rev. No.	CN No.	Effective Date	Description of Revision/CN
0		08/23/96	Initial Issue
0	TIP-CM-06-0-1	09/18/96	Text changes for clarification only; repagination. Affects Title Page, pages 3 through 7 of 7, and Appendix A.
0	TIP-CM-06-0-2	04/04/97	Addition of balance to acceptable list in Section 6.0; changes made in Procedure. Affects Title Page and pages 6 and 7 of 7.

Approved by: W. L. Clarke 4/3/97

CRWMS LLNL Manager **Date**

Approved by: Carni L Brumburgh for Royce Monks 4/3/97

M&O LLNL Quality Assurance Manager **Date**

Approved by: R Daniel McCright 3 April 1997

Technical Area Leader **Date**

1.0 PURPOSE

This procedure describes the formulation and make-up of Simulated Dilute Water (SDW), a low-ionic-content water to be used for Activity E-20-50 "Long-Term Corrosion Studies." This water has an ionic content which is nominally a factor of ten higher than that of "representative" waters at or near Yucca Mountain. "Representative" waters were chosen as J-13 well water [Harrar, 1990] and "perched" water at Yucca Mountain [Glassley, 1996] (see Table 1). J-13 well water is obtained from ground water that is in contact with the Topopah Spring tuff, which is the repository horizon rock. The "perched" water is located in the Topopah Spring tuff, but below the repository horizon and above the water table. A nominal times ten higher ionic content was chosen to simulate the effect of ionic concentrating due to elevated temperature water flowing through fractures where salts and minerals have been deposited due to evaporation and boiling.

The expected composition of the SDW is given in Table 1. It is anticipated that the actual composition of test solutions will be within ± 20% of these values. The changes in the corrosive properties of the test solutions will be acceptable within these values. In addition similar type materials are tested in the same test vessel, so minor vessel to vessel variation of solution composition is of limited significance.

Both of the "representative" waters have similar corrosive characteristics. The solution pH's and the concentrations of the aggressive anions (Cl^-, F^-, and SO_4^{2-}) are essentially equivalent from a corrosion stand point.

This aqueous solution is one of the four aqueous test solutions to be used in the activity. The other aqueous solutions included a Simulated Concentrated Water (SCW), a simulated acidic concentrated water (SAW), and a simulated basic concentrated water (SBW).

This TIP documents the chemical reagents, reactant air, and the procedures used to make-up the aqueous solution for Activity E-20-50. More than 12,000 liters (3,170 gallons) of Simulated Dilute Water solution are required for the test vessels for implementation of the full test matrix of the activity plan.

2.0 SCOPE

This procedure applies to the Simulated Dilute Water solution, one of the aqueous solutions that are to be used in the test vessels for Activity E-20-50 "Long-Term Corrosion Studies."

3.0 RESPONSIBILITIES

The Principal Investigator (PI) or designee is responsible for:

- the conduct of the activities and methods described in this procedure, and
- maintaining laboratory scientific notebooks.

The Task Area Leader (TAL) is responsible for:

- ensuring that the requirements of this procedure are implemented,
- ensuring that personnel conducting the work are qualified and are trained to this procedure,
- verifying that this procedure meets the objectives of the Scientific Investigation Plan (SIP) "Metal Barrier Selection and Testing" (SIP-CM-01, Rev.3, WBS # 1.2.2.5.1) and Activity E-20-50 "Long-Term Corrosion Studies", and
- ensuring approval of this procedure.

The YMP Quality Assurance Manager (QA Manager) is responsible for:

- monitoring the work to assure proper implementation of this procedure, and
- assuring its continued effectiveness.

4.0 COMPOSITION OF SDW AND REACTANT AIR

4.1 Aqueous Solution Composition

The Simulated Dilute Water (SDW) has a ionic composition that is nominally a factor of ten higher than that of "representative" water of Yucca Mountain. "Representative" waters were chosen J-13 well water [Harrar, 1990] and "perched" water at Yucca Mountain [Glassley, 1996]. J-13 well water is obtained from ground water that is in contact with the Topopah Spring tuff, which is the repository horizon rock. The "perched" water is located in the Topopah Spring tuff, but below the repository horizon and above the water table. The times ten higher ionic content was chosen to simulate a slight ionic concentrating due to water flowing through fractures where repeated evaporation and boiling has resulted in deposition of salts and minerals.

The composition of J-13 well water and the "perched" water are given in Table 1. Only ions with concentration greater than 0.5 ppm are included in this table. Minor constituents have been detected in J-13 well water; these include Li, B, Al, Mn, Fe, Sr, and PO_4^{3-} ions. These constituents have been reported in the 10-100 µg/liter concentration. The most consistently determined minor constituents are Li and B at a mean (several studies) concentrations of 48 and 134 µg/liter, respectively. The minor constituents are not explicitly included in the SDW. However, the reagent chemicals have some impurites, which may included the above noted impurities. **The minor constituents at the reported concentrations are not expected to significantly effect the corrosion of the test specimens.**

It is worth noting the differences in the "representative" waters. In terms of the calcium and bicarbonate concentrations, the "perched" water is higher in both of these constituents, and has a higher pH; these both are probably due to contact with calcium carbonate ($CaCO_3$) minerals. The concentrations of Na^+, K^+, F^-, and NO_3^- are slightly higher in J-13 well water.

Table 1. Compositions of "representative" Yucca Mountain waters J-13 well water and "perched" water, and the estimated composition of the simulated dilute water.

Constituent	J-13 (mg/l) (mg/l)	"Perched" (mg/l)	Simulated dilute water (estimated)
Na	45.80	36	409
Si	28.5	37	27 (60C); 49 (90C)
Ca	13.0	25	0.5
K	5.04	1.7	34
Mg	2.01	2.2	1
F^-	2.18	0.7	14
Cl^-	7.14	6.3	67
NO_3^-	8.78	4	64
SO_4^{2-}	18.4	15	167
HCO_3^-	128.9	147	947
$CaCO_3$	—	—	470 (precipitate)
$MgCO_3$			70 (precipitate)
pH	7.41	8.1	

The following paragraphs explain the reasoning used to arrive at the composition and formulation of the SDW. The silica content is based on solubility of α-cristobalite which is believed to be the dominant soluble silica phase of Yucca Mountain rock at 60 and 90°C [Wolery, 1983; Knauss, 1987]. Silica may be added to the solution by dissolution of sodium silicate, or the addition of colloidal silica. Most salts, in general, are concentrated by a factor of ten over an "average" of the "representative" Yucca Mountain waters. Calcite and magnesite precipitate upon concentrating the solution.

Simulations of concentrating the "representative" water have been run using the software "The Geochemist's WorkBench" [Bethke, 1994]. These simulations show that calcite ($CaCO_3$) and magnesite ($MgCO_3$) will precipitate with concentrating of the solution and their amounts remain approximately constant with temperature. The program predicts that about 470 mg/l of calcite and about 70 mg/l of magnesite will precipitate.

The estimated composition of the SDW is given in Table 1. It is expected that the actual composition of test solutions will be within ± 20% of these values. The changes in the corrosive properties of the test solutions within these values will not be significant. In addition similar type materials are tested in the same test vessel, so minor vessel-to-vessel variation of solution composition is of limited significance.

4.2 Reactant Air

Reactant air is compressed building air which has been purified to remove hydrocarbons and water. Air will be purified by flowing through a Whatman Zero Air Generator (see Section 6.0). Nominal flow rates through each test vessel will be 200 ml/min. Air will exit through a condenser to remove water; this greatly reduces the amount of water loss from the test vessels.

Reactant air serves two purposes: 1) it keeps the oxygen content of the vessels constant, and 2) the slightly pressurized test vessel will keep the potentially contaminated room air out of the test vessels.

5.0 REAGENTS AND FORMULATION

5.1 Reagent Chemicals

In order to obtain the solution composition given in Table 1, various combinations of chemicals can be used. A spreadsheet has been developed which calculates the composition of a solution based on the added chemicals. **Copies** of typical outputs of the spreadsheets **are** shown in Appendix A **for 60 and 90°C solutions; the amount of silica changes with temperature.** Many of the chemicals listed in the spreadsheet are not used in this particular example. The inclusion of numerous chemicals in the spreadsheet allows the user the freedom to choose the needed chemicals based on availability, cost, and personal preference.

The algorithm to arrive at reagent concentrations was a trial and error method. The quantities of reagents required was estimated, and the spreadsheet calculated the total ionic content of the theoretical solution. Iteration was continued until an acceptable match was achieved.

A few guidelines were used in choosing the reagents. The choice**s** for bicarbonate ions **were** $NaHCO_3$ **and $KHCO_3$,** since **these are** the common commercial source of bicarbonate. The use of potentially hazardous materials such as HF, MgF_2, and CaF_2 was avoided. The more soluble form of the salts was chosen, for example, magnesium sulfate was chosen over the less soluble carbonate and nitrate salts.

Also solution silica will be obtained by the addition of sodium silicate. (Calculations showed that dissolution of solid silica phases would take extended periods of time (>1000 days) in order for sufficient amounts of silica to dissolve.)

Using sodium silicate will result in the formation of hydroxyls equal to the number of moles of sodium atoms added. **In order to neutralize the hydroxyls, an equal number of moles of acid (hydrochloric, nitric, or sulfuric) will be added.**

Since a large percentage of both the calcium and magnesium will form carbonate precipitates, it was not necessary to add soluble salts of these ions to the level of the concentrating. However excess of these ions will be added such that precipitates of calcite and magnesite will form.

A word of caution in using the spreadsheet: the calculations assume that the chemicals dissolve completely and may therefore over estimate the composition of some species. The user must therefore be aware of potential solubility problems. A listing of the solubilities of various chemical is shown in Appendix B.

A typical example of chemicals used to make-up of the aqueous solution are listed in Table 2 along with the quantities required per 1000 l of solution.

Table 2. An example of the reagents and quantites required per 1000 liters of simulated aqueous solution.

Reagent	Quantity @ 60°C (gms / 1000 liters)	**Quantity @ 90°C (gms / 1000 liters)**
$NaHCO_3$	**1269.3**	**1137.8**
NaF	31.9	**31.9**
$Na_2SiO_3 \bullet 5H_2O$	**204.0**	**370**
$MgSO_4 \bullet 7H_2O$	214.0	**214.0**
$CaSO_4 \bullet 2H_2O$	**147.4**	**74.2**
$Ca(NO_3)_2 \bullet 4H_2O$	**121.7**	**37.4**
HCl	**69.1**	**69.1**
$KHCO_3$	**86.2**	**86.2**
$CaCO_3$	**337.2**	**415.6**
$H2SO_4$	**1.38**	**43.1**
HNO_3	----	**45.0**

The chemicals and the quantities used in making up the test solutions **will be listed in the Scientific Notebook, or electronic media.**

5.2 Purified Water

The make up of the test solutions requires large quantities of low ionic content water is required. The use of LLNL de-ionized water is acceptable. This water has an ionic content typically less than 1 ppm. This is less than 0.1% of the ionic content due to the added chemicals. The source of the water used in testing will be recorded in the scientific notebook.

5.3 Reactant Gas

The reactant air will be purified before entering the test vessels.

6.0 EQUIPMENT

A balance that can measure to 0.1 grams is acceptable for make-up of the test solutions. An acceptable balance is:

Mettler Balance Model # AT200
Serial Number 1114463500

Mettler Balance Model # PC16
Serial Number A51361

An air purifier for cleaning the building compressed air is required. The following unit or equivalent is acceptable:

Whatmann Type 76-818NA Zero Air Generator
Unit Serial Number 768180065B
Tower Module Serial Number 76811-10116B

This air purifier removes hydrocarbon to 0.1 ppm.

7.0 PROCEDURE

The following procedure will be followed in making-up of the Simulated Dilute Water solutions for the test vessels:

1) Purified water is emplaced in the cleaned vessel; the liquid level is slightly less than the required depth for testing. (Need to account for rise in water level due to the specimens and racks, and the density decrease due to raising the water temperature to the test temperature.)

2) The amount of purified water added to the test vessels is estimated.

3) The required amount of reagent chemicals is determined and entered in the scientific notebook or electronic media.

4) The purified water is heated to a nominal temperature of 40°C. This will accelerate reactions that occur in solution.

5) The water will be stirred. The stirrer mounted on the vessel is sufficient.

6) **Add chemicals to water. No particular order is required for chemical additions except that hydrochloric and sulfuric acid will be the last chemicals added to the test vessel.**

7) **Concentrated hydrochloric acid shall be diluted 500-1000 times the required volume using deionized water and then added to the test vessel.**

8) **Concentrated sulfuric acid shall be diluted 500-1000 times the required volume using deionized water and then added to the test vessel.**

9) **The vessel is sealed and brought to testing temperature for at least 24 hours.**

10) The specimen racks are inserted into test vessel.

11) A sample of the test solution is withdrawn for analysis approximately a day after the level of water reaches the normal operation set point.

Note: The liquid level in the test vessels will self-adjust to the required level. If the liquid level is low, the liquid level control system will add purified water. If the liquid level is high, water removal by the air purge will occur; this may be slow but it will occur. It is preferred to add water rather than to remove water, since the control system shuts down the heaters when the liquid level is above a certain height.

8.0 QA RECORDS

Any data that is pertinent to this TIP shall be entered into the Scientific Notebook or electronic media for Activity E-20-50. This shall include, but is not be limited to the chemical used lot # manufacturer supplied analysis, and actual reagent chemical amounts used for make-up.

9.0 REFERENCES

J.E. Harrar, J.F. Carley, W.F. Isherwood, and E. Raber, "Report of the Committee to review the Use of J-13 Well Water in Nevada Nuclear Waste Storage Investigations," Lawrence Livermore National Laboratory report UCID-21867, Livermore California, January 1990.

W. Glassley, private communication, 1996.

C.M. Bethke, The Geochemist's Workbench, Version 2.0; A Users Guide to Rxn, Tact, React, and Gtplot, Hydrogeology Program, University of Illinois, 1994.

K.G. Knauss, W.J. Beiriger, D.W. Peifer, "Hydrothermal Interaction of Solic Wafers of Topopah Spring Tuff with J-13 Water at 90 and 150°C Using Dickson-Type, Gold-Bag Rocking Autoclaves: Long-Term Experiments," Lawrence Livermore National Laboratory Report UCRL-53722, May 1987.

T.J. Wolery, Memo GCC-83-3/1773w, "Summary of Silica Solubility Data for Acid-to-Neutral pH Conditions," 16 Nov. 1983.

Compound	Mol Wt.	gms/ 1000 l	K	Na	Mg	Ca	Cl	F	HCO3	CO3	SO4	NO3	SiO3	H
NaCl	58.44	0.0		0.0			0.0							
NaOH	40.00	0.0		0.0										
NaHCO3	84.01	1269.3		347.4					921.9					
Na2CO3	105.99	0.0		0.0						0.0				
Na2SO4	142.04	0.0		0.0							0.0			
NaNO3	84.99	0.0		0.0								0.0		
Na2CO3	105.99	0.0		0.0						0.0				
NaF	41.99	31.9		17.5				14.4						
Na2SiO3•9H2O	284.20	0.0		0.0									0.0	
Na2SiO3•5H2O	212.14	204.0		44.2									73.2	
MgCl2•6H2O	203.31	0.0			0.0		0.0							
MgF2	62.31	0.0			0.0			0.0						
(MgCO3)4•Mg(OH)2(	485.69	0.0			0.0					0.0				
MgSO4	120.37	0.0			0.0						0.0			
MgSO4•7H2O	246.48	214.0			21.1						83.4			
Mg(NO3)2•6H2O	256.41	0.0			0.0							0.0		
CaCl2	110.99	0.0				0.0	0.0							
CaCl2•2H2O	147.02	0.0				0.0	0.0							
CaF2	78.08	0.0				0.0		0.0						
CaCO3	100.09	337.2				135.0				202.2				
CaSO4	136.14	0.0				0.0					0.0			
CaSO4•2H2O	172.17	147.4				34.3					82.2			
Ca(NO3)2•4H2O	236.15	121.7				20.7						63.9		
CaCO3MgCO3	184.41	0.0			0.0	0.0				0.0				
H2SO4	98.08	1.3800									1.4			0.0284
HCl	36.46	69.1					67.2							1.9103
HNO3	63.01	0.0										0.0		0.0000
KF•2H2O	94.13	0.0	0.0					0.0						
KCl	74.56	0.0	0.0				0.0							
K2SO4	174.27	0.0	0.0								0.0			
KNO3	101.11	0.0	0.0									0.0		
KHCO3	100.12	86.2	33.7						52.5					
K2CO3	138.21	0.0	0.0							0.0				
KOH	56.11	0.0	0.0											
i													73.2	
Totals			33.7	409.0	21.1	190.0	67.2	14.4	974.5	404.3	167.0	63.9	27.0	1.9386
Target			33.7	409.0	21.1	190.0	67.2	14.4	1379.5		167.0	63.9	27 (Si)	1.9386
										1379				
						[HCO3] + [CO3] + [OH] = 1379.5								

Compound	Mol Wt.	gms/ 1000 l	K	Na	Mg	Ca	Cl	F	HCO3	CO3	SO4	NO3	SiO3	H
NaCl	58.44	0.0		0.0			0.0							
NaOH	40.00	0.0		0.0										
NaHCO3	84.01	1137.8		311.4					826.4					
Na2CO3	105.99	0.0		0.0						0.0				
Na2SO4	142.04	0.0		0.0							0.0			
NaNO3	84.99	0.0		0.0								0.0		
Na2CO3	105.99	0.0		0.0						0.0				
NaF	41.99	31.9		17.5				14.4						
Na2SiO3•9H2O	284.20	0.0		0.0									0.0	
Na2SiO3•5H2O	212.14	370.0		80.2									132.7	
MgCl2•6H2O	203.31	0.0			0.0		0.0							
MgF2	62.31	0.0			0.0			0.0						
(MgCO3)4•Mg(OH)2•	485.69	0.0			0.0					0.0				
MgSO4	120.37	0.0			0.0						0.0			
MgSO4•7H2O	246.48	214.0			21.1						83.4			
Mg(NO3)2•6H2O	256.41	0.0			0.0							0.0		
CaCl2	110.99	0.0				0.0	0.0							
CaCl2•2H2O	147.02	0.0				0.0	0.0							
CaF2	78.08	0.0				0.0		0.0						
CaCO3	100.09	415.6				166.4				249.2				
CaSO4	136.14	0.0				0.0					0.0			
CaSO4•2H2O	172.17	74.2				17.3					41.4			
Ca(NO3)2•4H2O	236.15	37.4				6.3						19.6		
CaCO3MgCO3	184.41	0.0			0.0	0.0				0.0				
H2SO4	98.08	43.1									42.2			0.886
HCl	36.46	69.1					67.2							1.91
HNO3	63.01	45.0										44.3		0.72
KF•2H2O	94.13	0.0	0.0					0.0						
KCl	74.56	0.0	0.0				0.0							
K2SO4	174.27	0.0	0.0								0.0			
KNO3	101.11	0.0	0.0									0.0		
KHCO3	100.12	86.2	33.7						52.5					
K2CO3	138.21	0.0	0.0							0.0				
KOH	56.11	0.0	0.0											
													132.7	
Totals			33.7	409.0	21.1	190.0	67.2	14.4	879.0	498.4	167.0	63.9	49.0	3.516
Target			33.7	409.0	21.1	190.0	67.2	14.4	1379.5		167.0	63.9	49 (Si)	3.516
										1377				
						[HCO3] + [CO3] + [OH] = 1379.5								